Inverse Photoemission Observation of an Unoccupied Surface State on Pd(111)

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The energy dispersion curve $E(k_{\parallel})$ has been measured for an unoccupied sp-like surface state on Pd(111) with k-resolved inverse photoemission spectroscopy. At the zone center, $\bar{\Gamma}$, the energy of the surface state is 1.7 eV above the Fermi level, in good agreement with theoretical pseudopotential calculations of Louie, although the energy dispersion away from $\bar{\Gamma}$ is appreciably more rapid than in theory. The work opens up the possibility of probing unoccupied surface states in the same way that angle-resolved photoemission probes occupied surface states.

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It is now well established that surface states and their dispersion relations in energy versus parallel wave vector, $E(\vec{k}_{\parallel})$, can be investigated by means of angle-resolved ultraviolet photoemission spectroscopy (ARUPS). The limitation of such studies is that they provide information only on the occupied surface states. It has recently been demonstrated, in the study of bulk solids, that k-resolved inverse photoemission spectroscopy (KRIPES) can be used to map $E(k_{\parallel})$ relations in the unoccupied region just as ARUPS is used in the occupied region.[1] In this paper we report the first application of these methods to an unoccupied surface state. The results are compared and contrasted with available theoretical calculations.

The surface under investigation was Pd(111) which has previously been shown both theoretically[2] and experimentally[3] to be rich in occupied surface states. Theoretically it has been shown that the occupied surface states are predominantly d like in character[2] while the expected unoccupied surface state is sp like.[2,4]

The experimental apparatus used for this experiment is described elsewhere.[5] Briefly, inverse photoemission spectra at a fixed photon energy $\hbar\omega = 9.7$ eV are recorded as a function of the angle of incidence θ of the electron beam. This allows the dispersion of different peaks in the spectra to be mapped out as a function of $k_{\parallel}$. The Pd sample was cleaned by several cycles of argon bombardment and annealing.

Our ultraviolet KRIPES spectra recorded from the Pd(111) surface in the $\bar{\Gamma}\bar{K}$ azimuth of the surface Brillouin zone are shown in Fig. 1. Two peaks are clearly visible. Peak A, approximately 0.6 eV above the Fermi level E_F, is associated with the unoccupied part of the d band. At $\hbar\omega = 9.7$ eV no direct (k-conserving) transitions are permitted into the unoccupied Pd d band for $k_{\parallel} = 0$, although they do become possible with increasing $k_{\parallel}$. There is presumably a contribution also involving evanescent low-energy electron diffraction–type initial-state wave functions rather than bulk Bloch functions.[6] Peak B, which is found at 1.7 eV above the Fermi level for normal incidence, and which disperses rapidly away from the Fermi level for off-normal incidence, is believed to be the surface state predicted by theory.[2,4]

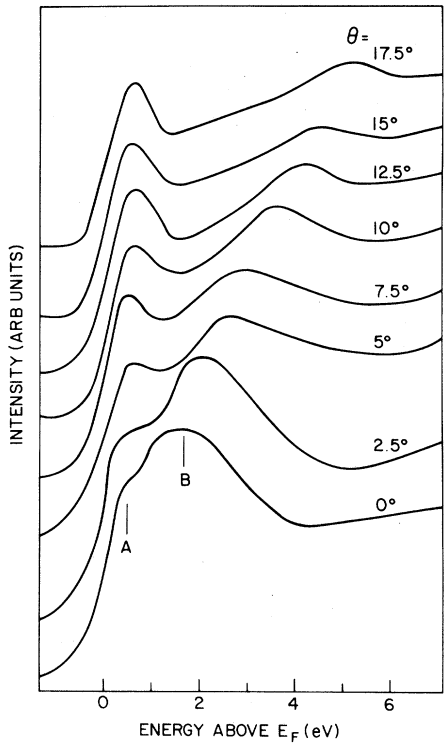

FIG. 1. Measured KRIPES spectra for different angles of electron incidence along the $\bar{\Gamma}\bar{K}$ azimuth on the Pd(111) surface. Peaks A and B are discussed in the text.

Evidence to support the surface nature of this state is provided by adsorption studies shown in Fig. 2. Here the KRIPES data recorded from the clean surface for an angle of incidence 7.5° off the surface normal in the $\bar{\Gamma}\bar{M}$ azimuth is compared with those taken after the surface had been exposed to 3 L [1 L (langmuir) = 10^{-6} Torr sec] of chlorine. It will be seen that the adsorption has removed peak B but peak A remains. This dependence on the state of surface cleanliness is a characteristic of a surface state. Also, the energy of the state falls in an absolute gap of the bulk band structure.

In Fig. 3 we compare the experimentally determined $E(k_{\parallel})$ dispersion curve with the theoretical results of Louie obtained using a self-consistent pseudopotential method. This surface state, which falls in the bulk $L_{2'}$-L_1 band gap and is found near $\bar{\Gamma}$, the center of the two-dimensional Brillouin zone, is the equivalent of the surface states known to exist on the noble-metal (111) surfaces.[4,7] On those surfaces, however, the state is occupied at $\bar{\Gamma}$ and therefore detectable in ARUPS. The observed energy of the Pd(111) surface state at $\bar{\Gamma}$, 1.7 eV above E_F, is in excellent agreement with theoretical results.[2,4] The closeness of this agreement is fortuitous because (a) the broadness of the structure does not permit a particularly precise location of its center (estimated precision ~0.1–0.2 eV, comparable with the size of the points plotted in Fig. 3); and (b) the theoretical calculations are nonrelativistic. At $\bar{\Gamma}$ the surface state lies a few tenths of an electronvolt above the bottom of the absolute bulk band gap (corresponding to the bulk energy level L_γ). In relativistic calculations,[8] this level (and presumably the surface state) lies about 0.7 eV closer to E_F.

The dispersion away from the Fermi level is more rapid in the experiment than theory. The theoretical dispersion is approximately free-electron like, whereas the experimental dispersion would be described by an effective mass ~0.5m. The experimental surface state, unlike in the theory, shows no tendency to move out of the absolute gap and become a surface resonance degenerate with bulk states. When we take into account the required relativistic correction mentioned above, the observed surface state is centered throughout at about 1 eV above the gap edge.

At first sight, the energy width of the surface state seems unexpectedly large. Figure 2 illustrates how, after a crude linear background subtraction, we obtain a full width at half maximum of 2.1 eV for the spectrum at $\theta = 7.5°$. This width remains fairly constant, although inspection of Fig. 1 may indicate some qualitative tendency for the peak to sharpen up with increasing energy. On the basis of the experience in ARUPS of surface states in the same energy range *below* E_F,[9] we would have expected an inherent width of ~0.5 eV. Only part of the width can be ac-

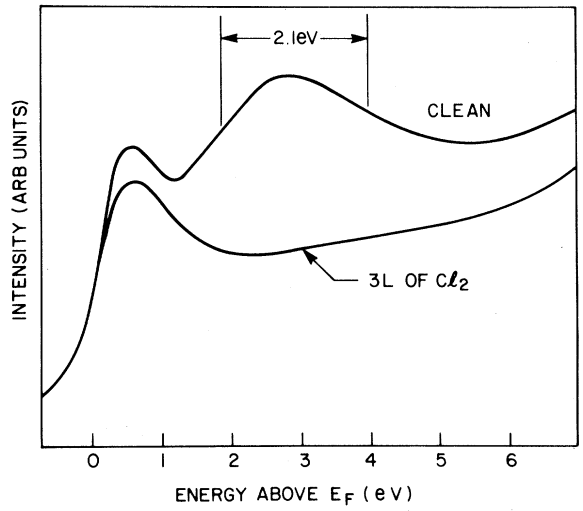

FIG. 2. Comparison of the KRIPES spectrum measured for the clean surface and the same surface after exposure to 3 L of Cl_2. The angle of electron incidence is 7.5° from the surface normal.

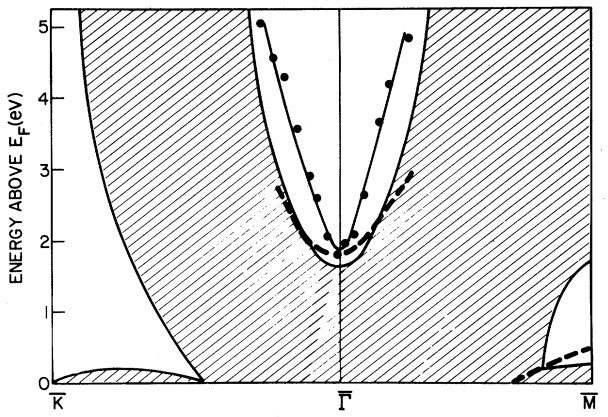

FIG. 3. Comparison of the experimentally observed $E(k_{\parallel})$ dispersion of the unoccupied surface state (full circles connected by a smooth curve) with the theoretical calculation of Ref. 2 (dashed curves). The hatched area is the projection of the bulk band structure onto the two-dimensional Brillouin zone.

counted for by the instrumental resolution of 0.7 -0.8 eV. Another part can be attributed to the instrumental angular resolution coupled to the rapidity of the energy dispersion; a reasonable estimate of the angular resolution would be 5° full width at half maximum, implying a further energy spread of ~0.8 eV. It is therefore quite possible that the residual width due to the inherent lifetime of the surface state is consistent with the above expectations. Clearly, experimental work at higher angular and energy resolution would be desirable to resolve this point.

In summary, we have extended the technique of KRIPES to the study of surface states. We have mapped the $E(k_{\parallel})$ relations for an unoccupied surface state on Pd(111)—information unobtainable in any other technique. In general, KRIPES promises to deliver the half of the information on surface states not accessible with use of ARUPS. Some particular questions concerning the energy width and dispersion of the Pd(111) surface state would be worthy of further investigation.

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Sliding Conductivity of Charge-Density Waves

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A classical model of charge-density wave motion at large velocities is used to describe the nonlinear response of the charge-density wave in fields well above the threshold. The charge-density wave is regarded as a charged, deformable medium and its interaction with pinning centers is treated in perturbation theory. The results fit the available high-field data on $NbSe_3$ well. The observed interference effects between a large dc field and an ac field are also explained.

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Peierls and Fröhlich[1] showed how the coupling between conduction electrons and the phonons of an anisotropic metal could lead to a charge-density wave (CDW): a periodic modulation of the electron density and a corresponding distortion of the lattice. Fröhlich also suggested that a CDW could slide and carry electrical current. This phenomenon has now been observed[2,3] in $NbSe_3$; the CDW is pinned at small electric fields but moves in the presence of fields larger than a threshold depinning field.[4] This results in a nonlinear current-voltage curve,[2,3] which has to date been analyzed in terms of both a single classical degree of freedom[5] (or "particle") and a Zener-tunneling model.[6] The latter theory involves the quantum mechanical tunneling of macroscopic portions of the CDW, which we believe implausible. Neither theory is consistent with all of the data.[7]

The purpose of this Letter is firstly to present a model which we believe is a more realistic and complete model of a moving CDW than has been given to date. It is classical and includes the internal degrees of freedom of the CDW. Secondly